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Hole doping into Co-12*s*2 copper oxides with *s* fluorite-structured layers between CuO_2 planes

H. Fjellvåg[a,b], Y. Morita[a], T. Nagai[c], J.-M. Lee[d], J.-M. Chen[d], R.-S. Liu[e], B.C. Hauback[f], V.P.S. Awana[a,g], Y. Matsui[c], H. Yamauchi[a], M. Karppinen[a,*]

[a]*Materials and Structures Laboratory, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226-8503, Japan*
[b]*Centre for Materials Science and Nanotechnology, University of Oslo, N-0315 Oslo, Norway*
[c]*National Institute for Materials Science, 1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan*
[d]*National Synchrotron Radiation Research Center, Hsinchu, Taiwan, ROC*
[e]*Department of Chemistry, National Taiwan University, Taipei, Taiwan, ROC*
[f]*Institute for Energy Technology, N-2027 Kjeller, Norway*
[g]*National Physical Laboratory, Krishnan Matg, New Delhi 12, India*

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Abstract

In this work, the first three members ($s = 1, 2, 3$) of the Co-12*s*2 homologous series of multi-layered copper oxides are gradually doped with holes through high-pressure oxygenation (HPO). The phases differ from each other only by thickness of the fluorite-structured layer block, (Ce,Y,Ca)–$[O_2$–(Ce,Y)$]_{s-1}$, between two identical CuO_2 planes. High-resolution transmission-electron microscopy (HRTEM) and electron diffraction (ED) analyses together with both synchrotron X-ray and neutron powder diffraction data, reveal that as a consequence of HPO the charge-reservoir CoO_4-tetrahedra chains get broken and the lattice symmetry of the Co-12*s*2 phases changes from orthorhombic to tetragonal. Oxygen contents are analyzed for the samples with wet-chemical and thermogravimetric techniques. The valence state of copper in the CuO_2 plane is determined from Cu *L*-edge X-ray absorption near-edge structure (XANES) spectra to be compared with the values estimated through bond-valence-sum (BVS) calculations from the crystal structure data. The positive charge induced by oxygen loading (or aliovalent Ca^{II}-for-Y^{III} substitution in $CoSr_2YCu_2O_{7+\delta}$) is found not to be completely accommodated in the CuO_2 planes but be rather effectively trapped at the charge-reservoir Co atoms. Superconductivity appears in the Co-1212 ($CoSr_2YCu_2O_{7+\delta}$) samples with the copper valence of 2.13 or higher, whereas in the Co-1222 ($CoSr_2(Ce_{0.25}Y_{0.75})_2Cu_2O_{9+\delta}$) and Co-1232 ($CoSr_2(Ce_{0.67}Y_{0.33})_3Cu_2O_{11+\delta}$) samples Cu valence does not increase high enough to induce superconductivity.
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1. Introduction

To date more than hundred different copper-oxide phases that show high-T_c superconductivity in their hole-doped CuO_2 plane(s) have been discovered. The high-T_c superconductor characteristically has a layered crystal structure in which the superconductive CuO_2 plane(s) alternate with non-stoichiometric and non-superconductive layers, the latter playing a dual role of a "spacing provider" and a "redox controller" for the former. There also exist a large number of related multi-layered copper-oxide phases for which superconductivity has not been observed yet. In order to comprehend the occurrence of high-T_c superconductivity in many of the complex copper oxide phases it is also essentially important to search for routes that might "superconductorize" some of the relevant candidate phases and then rationalize the reasons for the occurrence/absence of superconductivity in such phases. A majority of the not-yet-superconductorized but potential high-T_c superconductors are phases that belong to so-called "Category-B" [1,2]: they contain an additional fluorite-structured layer-block

*Corresponding author. Fax: +81 45 924 5365.
E-mail address: karppinen@msl.titech.ac.jp (M. Karppinen).

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of (Ce,*R*)–[O_2–(Ce,*R*)]$_{s-1}$ (*R* = rare earth element; valence states of Ce^{IV} and R^{III} are assumed) between two CuO_2 planes (i.e., the basal planes of corner-linked CuO_5 square-pyramid layers). The Category-B phase obeys the general formula of $M_mA_2(Ce,R)_sCu_2O_{m+4+2s\pm\delta}$ (*M* = Cu, Pb, Tl, Hg, etc.; *A* = Ba, Sr, etc.) expressed in short as *M*-*m*2*s*2 [2].

We recently synthesized samples of a three-fluorite-layer (*s* = 3) phase, Co-1232 of the composition of $CoSr_2(Ce_{0.67}Y_{0.33})_3Cu_2O_{11+\delta}$ [3,4]. Together with two previously known phases, Co-1212 ($CoSr_2YCu_2O_{7+\delta}$) [5–7] and Co-1222 ($CoSr_2(Ce_{0.4}Nd_{0.6})_2Cu_2O_{9+\delta}$) [8,9], the *s* = 3 phase forms a homologous series of Co-12*s*2 of Category-B (Fig. 1). In these phases two adjacent CuO_2 planes are separated from each other by a single *R*-cation layer for *s* = 1, a "double-fluorite-layer" block of (Ce,*R*)–O_2–(Ce,*R*) for *s* = 2, and a "triple-fluorite-layer" block of (Ce,*R*)–O_2–(Ce,*R*)–O_2–(Ce,*R*) for *s* = 3. It should be noted that the first member of the series, i.e., Co-1212, is isostructural with the $CuBa_2RCu_2O_{7-\delta}$ phase (Cu-1212 or "*R*-123") in terms of the layer sequence, *A*O-$MO_{1\pm\delta}$-*A*O-CuO_2–*R*–CuO_2. When synthesized by solid-state reaction in air, the single-phase samples of the three Co-12*s*2 phases are all essentially stoichiometric in terms of oxygen content, i.e., $\delta \approx 0$ for the $CoO_{1+\delta}$ "charge reservoir" [3]. Moreover it is known that, at $\delta = 0$ the charge reservoir of all the three Co-12*s*2 phases consists of zigzag chains of corner-linked CoO_4 tetrahedra that run diagonally relative to the perovskite base. Precise electron diffraction (ED) and high-resolution transmission-electron microscopy (HRTEM) studies have furthermore revealed a superstructure originating from a regular alternation of two zigzag chains that are mirror images of each other [4,6].

As-air-synthesized samples of Co-12*s*2 do not show superconductivity [3–9]. However, by taking advantage of a high-pressure oxygenation (HPO) technique we recently succeeded in making $CoSr_2(Y,Ca)Cu_2O_{7+\delta}$ samples of the Co-1212 phase superconductive [10]. At the same time, it was found that aliovalent Ca^{II}-for-Y^{III} substitution alone could not induce superconductivity. In the present work the HPO technique was first employed to introduce excess oxygen into the higher members of the Co-12*s*2 homologous series, i.e., Co-1222 and Co-1232. It turned out that even though excess oxygen was successfully loaded into these phases, it did not induce superconductivity. Therefore, the next goal was to elucidate reasons for this. Additionally, searched were possible reasons why

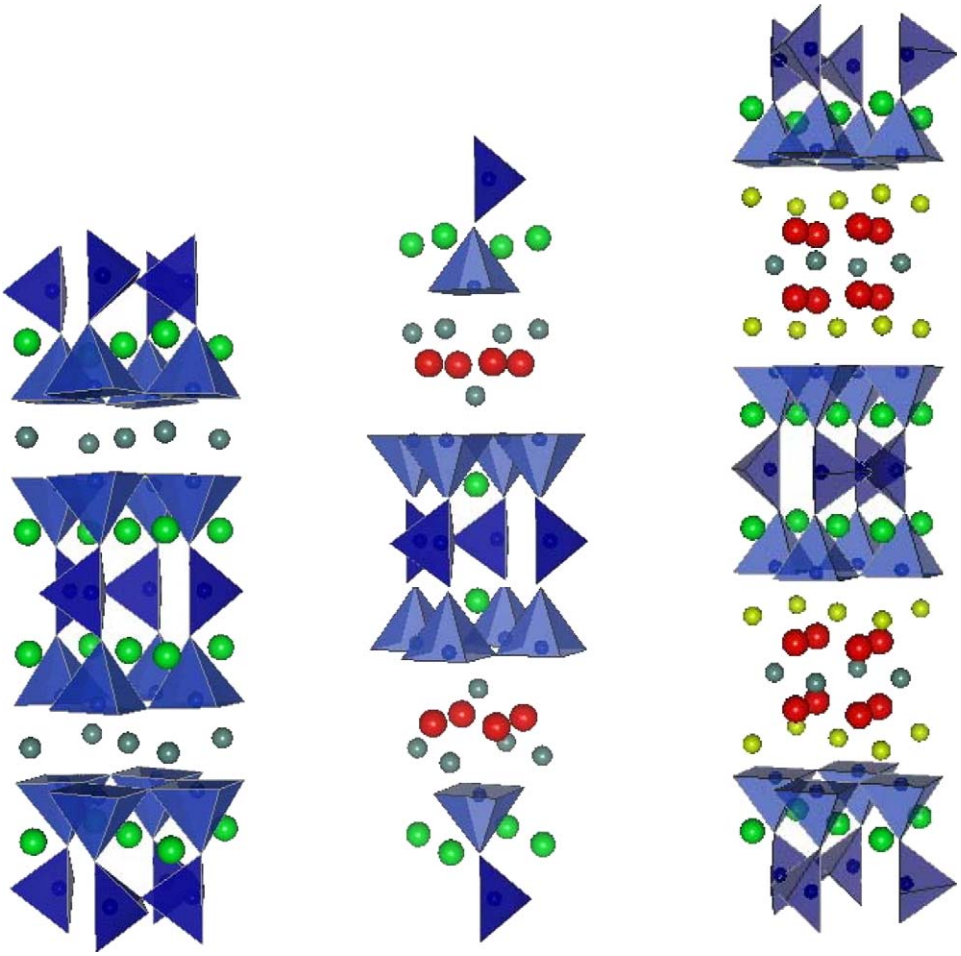

Fig. 1. Crystal structures of the first three members of the Co-12*s*2 homologous series.

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